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Ruthenium-Catalyzed Hydrosilation Copolymerization of Aromatic α,ω-Diketones with 1,3-Tetramethyldisiloxane

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Introduction

The hydrosilation reaction usually involves the platinum-catalyzed addition of a Si−H bond across a C=C double bond.[1] This reaction has been successfully applied to the preparation of a number of poly(carbosilanes) which contain Si−C bonds in their backbones.[2−4] Similar reactions between 1,3-tetramethyldisiloxane and α,ω-dienes have been used to prepare copoly(carbosilane/siloxanes) which contain both Si−C and Si−O bonds in their backbones.[5−7]

On the other hand, while the transition-metal-catalyzed hydrosilation reactions between ketones or aldehydes and silanes to yield silyl ethers have been known for more than twenty-five years, they have not been applied in polymer synthesis. While nickel was the first catalyst reported for this reaction in monomer systems, [8] more recently tris(triphenylphosphine)rhodium chloride or tris(triphenylphosphine)ruthenium dichloride catalysts have been used.[9−11] Tris(triphenylphosphine)ruthenium dichloride is less effective[11] unless it is activated by addition of an equimolar amount of silver trifluoroacetate.[12] The reason the rhodium- or ruthenium-catalyzed hydrosilation reactions have not been applied to polymer synthesis is not obvious. It is possible that the less than quantitative yields of silyl ethers generally reported in monomer systems have discouraged application of these reactions to polymer systems since close to quantitative yields are necessary if one is to obtain high molecular weight polymers in a step-growth process.

Polymeric silyl ethers, which have Si−O−C bonds in their backbones, have been prepared in several ways. Among this is the transetherification reaction between dialkoxysilanes and α,ω-diols.[13−15] The reaction of dichlorosilanes with α,ω-diols is not suitable because HCl catalyzes the hydrolysis of the C−O−Si bond system.[16] Poly(silyl ethers) have also been prepared by acid-catalyzed ring opening polymerization of 1-oxa-2-silacyclopentanes which have been obtained by platinum-catalyzed intramolecular hydrosilation of dimethylsilyl allyl ethers (Figure 1).[17]

Recently poly(silyl ethers) have been prepared by the reaction of dichlorosilanes with bis(glycidyl) ethers. Quarternary alkylammonium or phosphonium halides catalyze the reaction. Nucleophilic attack by halide ion on the strained ring of the epoxide results in ring opening and formation of a halomethyl group and a secondary alkoxide which in turn reacts with the silyl halide to form a Si−O−C silyl ether bond and regenerate the halide catalyst (Figure 2).[18−20]

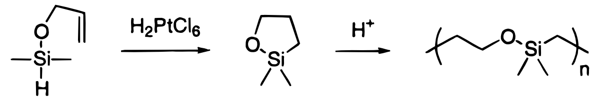

Figure 1. Poly(silyl ethers) obtained by ring-opening polymerization of 1-oxa-2-silacyclopentanes.

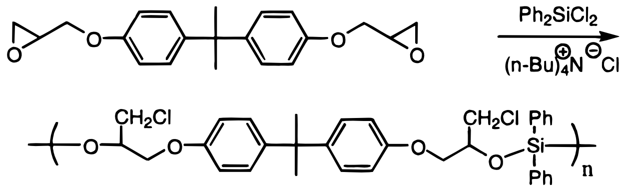

Figure 2. Poly(silyl ether) obtained by reaction of bis(glycidyl) ethers with dihalosilanes.

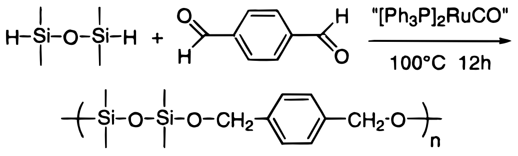

Figure 3. Ruthenium-Catalyzed hydrosilation polymerization of terephthaldehyde and 1,3-tetramethyldisiloxane.

Results

We should like to report the step-growth hydrosilation copolymerization of 1,4-diacetyldiphenyl ether, 1,4-diacetylbenzene, or terephthaldehyde with 1,3-tetramethyldisiloxane catalyzed by dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru), which has been activated by prior treatment with a stoichiometric amount of styrene.[21] These reactions provide an almost quantitative yield of copoly[1,1′-oxa-4,4′-diphenylene/1,3,3,5,5,7-hexamethyl-2,4,6- trioxa-3,5- disila-1,7-heptanylene] (**I**), copoly[1,4-phenylene/1,3,3,5,5,7-hexamethyl-2,4,6- trioxa-3,5-disila-1,7-heptanylene] (**II**), and copoly[1,4-xylenylene/2,2,4,4-tetramethyl-1,3,5-trioxa-1,5-pentanylene] (**III**), respectively. A similar copolymerization reaction between 1,4-diacetylbenzene and 1,3-tetramethyldisiloxane catalyzed by tris(triphenylphosphine)rhodium chloride gave a high yield of copolymer II of somewhat lower molecular weight. On the other hand, chloroplatinic acid was ineffective as a catalyst for this copolymerization reaction (Figure 3).

Experimental Section

^{1}H, ^{13}C, and^{29}Si NMR spectra were obtained on a Bruker AMX-500 MHz spectrometer operating in the FT mode. ^{1}H and^{13}C NMR spectra were run on 5% w/v chloroform-*d* solutions. Twenty-five percent w/v solutions in acetone-d_6 were used to obtain ^{29}Si NMR spectra.^{13}C NMR spectra were obtained with broad-band proton decoupling. A heteronuclear gated decoupling pulse sequence (NONOE) with a 60 s delay was used to acquire ^{29}Si NMR spectra.

Residual chloroform was used as an internal standard for ^{1}H and ^{13}C NMR.^{29}Si NMR spectra were referenced to an external TMS standard. IR spectra of neat films on NaCl plates were recorded on a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. UV spectra were run on cyclohexane solutions on a Shimadzu UV-260 spectrometer.

GPC analysis of the molecular weight distribution of the polymers was performed on a Waters system equipped with a R401 refractive index detector. Two 7.8 mm × 300 mm Styragel columns packed with <5 μm divinylbenzene cross-linked polystyrene HR4 and HR2 in series were used for the

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analysis. The eluting solvent was toluene at a flow rate of 0.3 mL/min. The retention times were calibrated against known monodisperse polystyrene standards: (929 000; 212 400; 47 400; 13 700; 794).

TGA of the polymers was measured on a Shimadzu TGA-50 instrument at a flow rate of 40 cm^3 of nitrogen per min. The temperature program was 4 °C/min from 25 to 750 °C. T_g of the polymer was determined by DSC on a Perkin-Elmer DSC-7. The DSC was calibrated by the melting point of indium, 156.6 °C. The temperature program for the analysis was begun at −100 °C. The temperature was increased at a rate of 10 °C/min to 50 °C.

1,4-Diacetylbenzene, terephthaldehyde, diphenyl ether, ruthenium trichloride hydrate, tris(triphenylphosphine)rhodium chloride, and styrene were purchased from Aldrich. 1,3-Tetramethyldisiloxane was obtained from Gelest. Chloroplatinic acid was obtained from Alfa.

Elemental analysis was done by Oneida Research Services Inc. Whitesboro, NY.

All reactions were conducted in flame-dried glassware under an atmosphere of argon.

Dihydridocarbonyltris(triphenylphosphine)ruthenium was prepared from ruthenium trichloride hydrate.[22]

4,4′-Diacetyldiphenyl ether was prepared by Friedel−Crafts acylation of diphenyl ether with 3 equiv of acetyl chloride and 2 equiv of aluminum chloride in carbon disulfide. It was recrystallized from ethanol; mp 100−101 °C.[23]

Activation of Dihydridocarbonyltris(triphenylphosphine)ruthenium (Ru). Ru (6.5×10^{-5} mol, 0.06 g), toluene (0.3 mL), styrene (7.5 μL, 6.5×10^{-5} mol, 6.8 mg), and a Teflon-covered magnetic stirring bar were placed in a 20 mL Ace pressure tube. The tube and its contents were seal and heated at 135 °C for 5 min. The color of the activated catalyst solution is red.[21] The tube was cooled to room temperature and was opened under argon.

Copoly[1,1′-oxa-4,4′-diphenylene/1,3,3,5,5,7-hexamethyl-2,4,6-trioxa-3,5-disila-1,7-heptanylene] (I). 4,4′-Diacetyldiphenyl ether (7.4 mmol, 1.89 g), and 1,3-tetramethyldisiloxane (7.4 mmol, 1.0 g) were added to a solution of activated catalyst in an Ace pressure tube. The tube and its contents were sealed and heated to 135 °C for 3 h. During the polymerization reaction, the color of the solution is brown. After 3 h, the color of the solution turned red, similar to that of the initially activated catalyst solution. The reaction was stopped at this point. After the reaction was cooled to room temperature, the polymer was dissolved in a minimum amount of THF and was precipitated from methanol three times. In this way, 2.7 g (93% yield) of polymer, $M_w/M_n = 49\,700/26\,970$, was obtained. The T_g of this material was −18 °C.^{1}H NMR, δ: −0.03 (s, 3H), −0.015 (s, 3H), 0.05 (s, 3H), 0.06 (s, 3H), 1.41 (dd, 6H, J = 5 and 1.5 Hz), 4.92 (qd, 2H, J = 6.5 and 2 Hz), 6.91 (d, 4H, J = 9 Hz), 7.23 (dd, 4H, J = 9 and 2 Hz). ^{13}C NMR, δ: −0.61, −0.62, −0.42, −0.40, 26.74, 69.76, 118.43, 126.67, 141.07, 156.18. ^{29}Si NMR, δ: −13.66. IR ν: 2972, 2927, 2890, 2869, 1602, 1502, 1450, 1413, 1370, 1260, 1240, 1117, 1092, 1059, 1033, 965, 848, 801 cm^{-1}. UV λ_{max}, nm (ϵ): 276 (3050), 268 (3040), 232 (16 900). Anal. Calcd for $C_{20}H_{28}O_4Si_2$: C, 61.81; H, 7.26. Found: C, 62.46; H, 7.44.

Copoly[1,4-phenylene/1,3,3,5,5,7-hexamethyl-2,4,6-trioxa-3,5-disila-1,7-heptanylene] (II). 1,4-Diacetylbenzene (2.415 g, 14.9 mmol), 1,3-tetramethyldisiloxane (2.0 g, 14.9 mmol), toluene 0.2 mL, and 25 μL (0.1 M in toluene) of activated Ru catalyst as above were placed in an Ace pressure tube. The tube was purged with argon, sealed, and heated to 100 °C in an oil bath. After 30 min, the 1,4-diacetylbenzene had dissolved. The tube was opened and an additional 50 μL of catalyst solution was added and the tube resealed. The color of the reacting solution was brown. After 12 h at 130 °C, the color of the solution had become red. The tube was opened, and the polymer was purified as above. In this way, 4.2 g (95.1% yield) of polymer with $M_w/M_n = 86\,180/24\,700 = 3.49$, T_g −55 °C, was obtained.^{1}H NMR, δ: 0.03 (s, 3H), 0.045 (s, 3H), 0.11 (s, 3H), 0.13 (s, 3H), 1.47 (d, 6H, J = 7 Hz), 5.01 (q, 2H, J = 6 Hz), 7.32 (s, 4H). ^{13}C NMR, δ: −0.78, −0.75, −0.61, −0.57, 26.69, 69.89, 69.90, 124.96, 144.68. ^{29}Si NMR, δ: −13.63. IR: ν 2972, 2928, 2889, 2868, 1688, 1443, 1413, 1370, 1260, 1210, 1098, 1053, 1035, 965, 848, 801 cm^{-1}. UV λ_{max}, nm (ϵ): 247 (959). Anal. Calcd for $C_{14}H_{24}O_3Si_2$: C, 56.71; H, 8.16. Found: C, 56.53; H, 8.18.

Copolymer II Obtained by Tris(triphenylphosphine)rhodium Chloride Catalysis. 1,3-Tetramethyldisiloxane (1.66 g, 12 mmol), 1,4-diacetylbenzene (2.00 g, 12 mmol), 250 μL of toluene, and tris(triphenylphosphine)rhodium chloride (20 mg, 20 μmol) were sealed in an Ace pressure tube under argon and heated at 130 °C for 12 h. The molecular weight of copolymer **II** was found to be $M_w/M_n = 48\,650/13\,830 = 3.52$. The spectroscopic properties of copolymer II were identical with those reported above.

Copoly[1,4-xylenylene/2,2,4,4-tetramethyl-1,3,5-trioxa-1,5-pentanylene] (III). Terephthaldehyde (2.09 g, 14.9 mmol), 1,3-tetramethyldisiloxane (2.0 g, 14.9 mmol), toluene (1 mL), and 25 μL (0.2 M in toluene) of activated Ru catalyst as above were placed in an Ace pressure tube. The tube was purged with argon, sealed, and heated to 100 °C in an oil bath. After 30 min, the tube was opened and an additional 50 μL of catalyst solution was added and the tube resealed. The color of the reacting solution was yellow. After 12 h at 100 °C, the tube was opened and the volatile solvents removed by evaporation under reduced pressure. A quantitative yield of **III**, $M_w/M_n = 93\,400/34\,100 = 2.74$, $T_g = -70$ °C, was obtained. ^{1}H NMR, δ: 0.247 (s, 12H), 4.86 (s, 4H), 7.40 (s, 4H). ^{13}C NMR, δ: −0.79, 64.41, 126.95, 140.44. ^{29}Si NMR, δ: −11.58. IR ν: 3022, 2962, 2867, 1515, 1462 1422 1414 1376 1260, 1214 1119 1089, 1052, 1019, 861, 802, 757 cm^{-1}. UV λ $_{max}$ nm (ϵ): 250 (617). Anal. Calcd for $C_{12}H_{20}O_3Si_2$: C, 53.69; H, 7.51. Found: C, 53.66, H, 7.64.

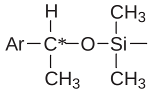
Discussion

Synthesis. Treatment of the catalyst dihydridocarbonyltris(triphenylphosphine)ruthenium with styrene serves to activate the catalyst by creating a site of coordinate unsaturation by removal of hydrogen from the ruthenium center.[21] This process may be analogous to the treatment of tris(triphenylphosphine)ruthenium dichloride with silver trifluoroacetate.[12] Apparently, the activated ruthenium catalyst we have utilized is at least as effective as tris(triphenylphosphine)rhodium chloride in these step-growth hydrosilation copolymerization reactions.

Copolymers **I**−**III** have not only silyl ether C−O−Si bonds but also disiloxane Si−O−Si bonds in their backbones. It is well-known that C−O−Si bonds are much more susceptible to acid- or base-catalyzed hydrolysis than Si−O−Si bonds.[24] The ruthenium-catalyzed hydrosilation copolymerization reaction reported here occurs under completely neutral conditions. This may account for the high yields of high molecular weight polymers obtained.

NMR. As expected, the ^{1}H, ^{13}C, and ^{29}Si NMR of the aromatic silyl ether polymer **III** is quite simple. Thus three singlets are observed in the ^{1}H NMR, four signals in the ^{13}C, and a single resonance in the ^{29}Si NMR spectra.

The ^{1}H and ^{13}C NMR of the two other aromatic silyl ether polymers, **I** and **II**, are complicated due to the presence of chiral centers. Thus the Ru-catalyzed addition of the Si−H bond across the C−O double bond of the acetyl group of 4,4′-diacetyldiphenyl ether, or 1,4-diacetylbenzene results in formation of a chiral center



$$\mathrm{Ar{-}\overset{\displaystyle H}{\underset{\displaystyle CH_3}{C^*}}{-}O{-}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{Si}}{-}}$$

The two methyl groups on silicon are adjacent to the

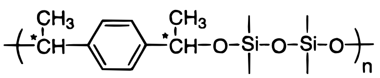


Figure 4. Chiral centers in copoly[1,4-phenylene/1,3,3,5,5,7-hexamethyl-2,4,6-trioxa-3,5-disila-1,7-heptanylene].

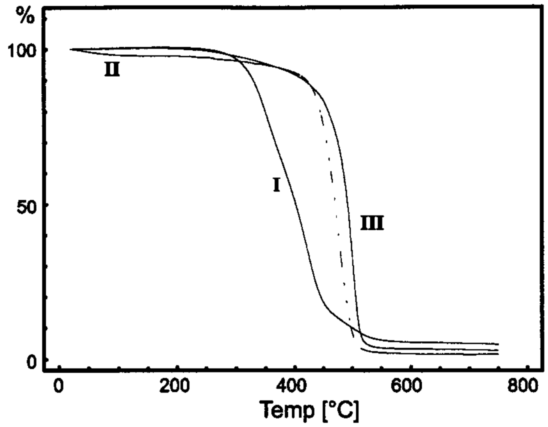


Figure 5. TGA of copolymers **I**–**III**.

chiral center and are diastereotopic.[25,26] Each unit of the polymer, in fact, contains two chiral centers. The stereochemical relationship of these to one another can either be *RR*, *SS*, or *RS* (meso). This results in four different stereochemical environments for the methyl groups on silicon (Figure 4).

Methanolysis. Silyl ethers are well-known to undergo both acid- and base-catalyzed hydrolysis and methanolysis. In general silyl ethers are more susceptible to acid-catalyzed hydrolysis and methanolysis than to basic hydrolysis.[27,28] The rate of these reactions depends not only on the concentration of acid or base but also on the nature of the substituents bonded to silicon and on the character of the alkyl or aryl group of the ether. In particular, if the carbon of the Si–O–C bond is secondary, the silyl ether is considerably more resistant to hydrolysis and methanolysis than if it is primary.[16] As expected, there are significant differences in stability to methanolysis among the poly(silyl ethers) **I**–**III**. Thus polymer **III**, in which the carbon atoms bonded to oxygen are primary, is unstable to precipitation from methanol. It undergoes rapidly methanolysis at room temperature. On the other hand, polymers **I** and **II** can be purified by precipitation from methanol. Samples of **II** have been stirred at 20 °C in a 80:20 mixture of THF–methanol for 3 days. No change in either the molecular weight or its molecular weight distribution of the sample was observed. Similar results were obtained with polymer **I**. Clearly, methanolysis of polymers **I** and **II** is not a rapid reaction at room temperature.

Closely related polymeric silyl esters which have a CO_2–Si bond system have been recently reported.[29–31] These have been prepared by transesterification reactions between α,ω-bis(trimethylsilyl) esters and α,ω-dichlorosilanes. As expected, the CO_2–Si bonds of these have been shown to be hydrolytically unstable. It has been suggested that this instability may make them useful for controlled drug release.[32] Likewise, the C–O–Si silyl ether bonds in copolymers **I**–**III** constitute a weak link which may provide controlled degradation by hydrolysis.

Thermal Stability. The polymeric aromatic silyl ethers **II** and **III** are more thermally stable than the aromatic poly(silyl ether) I. Polymer **I** is thermally stable to almost 300 °C. Above 300 °C, rapid catastrophic decomposition occurs. By 400 °C only 50% of the initial sample remains. By 450 °C only 15% is still present. Above 500 °C, slow weight loss occurs. By 750 °C a residue amounting to 5% is found. Poly(silyl ethers) **II** and **III** are thermally stable to about 300 °C. Between 300 and 400 °C approximately 7% of the initial sample weight is lost. Above 400 °C, rapid catastrophic decomposition occurs. By 520 °C, virtually no residue is left (Figure 5).

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